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RESEARCH MEMORANDUM

CHEMICAL AND PHYSICAL PROPERTIES OF HI-CAL-2

By A. E. Spakowski, Harrison Allen, Jr., and Robert M. Caves

Lewis Flight Propulsion Laboratory
Cleveland, Ohio

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

RESEARCH MEMORANDUM

CHEMICAL AND PHYSICAL PROPERTIES OF HI-CAL-2

By A. E. Spakowski, Harrison Allen, Jr., and Robert M. Caves

SUMMARY

The following chemical and physical properties were determined from a sample of Hi-Cal-2:

Elemental chemical analysis, percent	
Boron	53.60
Carbon	32.33
Hydrogen	13.51
Net heat of combustion of liquid fuel to gaseous carbon dioxide and water and solid boric oxide at 25° C,	
Btu/lb	-23,159
Density, g/ml	
at 20° C	0.841
at 25° C	0.838
Freezing point	No true freezing point found
Self ignition temperature, °C	125
Flash point, °C	17
Vapor pressure curve	$\log P_{mm} = - \frac{7825}{2.303RT_{abs}} + 6.240$
Extrapolated boiling point, °C	236
Decomposition, °C	>160

INTRODUCTION

As part of the Navy Project Zip to consider various boron-containing materials as possible high-energy fuels, the chemical and physical properties of Hi-Cal-2 prepared by the Callery Chemical Company were evaluated at the NACA Lewis laboratory. Elemental chemical analysis, heat of combustion, vapor pressure and decomposition, freezing point, density, self ignition temperature, flash point, and blow-out velocity were determined for the fuel. Although the precision of measurement of these properties was not equal to that obtained for hydrocarbons, this special release research memorandum was prepared to make the data available as soon as possible.

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PROCEDURE AND RESULTS

Chemical analysis. - The material, Hi-Cal-2, was handled either in a helium inerted dry box or under an atmosphere of helium to insure against any oxidation prior to analysis. The dark, straw-colored liquid was filtered as it was transferred from the original shipping container to smaller steel cylinders. The filter, when cleaned, was found to contain nylon-type fibers, iron filings, a yellow gelatinous mass, and other unidentified foreign matter.

The elemental chemical analysis followed the procedures set forth by Project Zip Standard Test Specifications Committee (ref. 1). Total carbon and hydrogen were determined by the microcombustion train to be 32.33 and 13.51 percent, respectively. Total boron, using the nitric acid oxidation method, was found to be 53.60 percent. These values, together with the standard deviations, are listed in table I.

Heat of combustion. - A Parr Adiabatic oxygen bomb calorimeter was used to determine the heat of combustion. The procedure to obtain the raw heat of combustion follows the general method recommended by the Parr Instrument Company with modifications as described in reference 2. In addition, another modification has been made to aid the combustion of boron and carbon. The lid of the adiabatic bomb was fitted with a fine platinum tube so that a burst of oxygen was directed onto the burning fuel at the moment the glass ampule burst. In some cases, this has increased the combustion efficiency of boron as much as 10 percent and carbon 5 percent. The bomb is calibrated with the oxygen line in place and a correction is made for the heat added to the bomb by the compression of the additional oxygen. The results from two determinations of Hi-Cal-2, including the analyses of the combustion products and the corrections applied to the raw heating values, are listed in table II. The average net heat of combustion of Hi-Cal-2 was -23,159 Btu per pound based on 25° C reference temperature.

Density. - The density was determined in an open-arm bicapillary pycnometer with ground-glass connections that were used to effect a seal to the atmosphere. The pycnometer was filled in a dry-box using helium as the inert gas after which the density measurements were made in the customary manner at two temperatures, 20° and 25° C. The densities were 0.841 and 0.838 gram per millileter, at 20° and 25° C, respectively. There is some uncertainty in these values because gas bubbles formed in the fluid during the measurements.

Freezing point. - The freezing point was determined in an apparatus featuring a closed sample system, electromagnetic stirrer, and a platinum resistance thermometer (ref. 3). No true freezing point was obtained. However, upon cooling the sample to -66.4° C, the stirrer was stopped by the increased viscosity of the sample. Further cooling with liquid nitrogen produced only a brittle glass-like material. No temperature measurement was taken at this point.

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Self ignition temperature. - The self ignition temperature was determined in the Setchkin apparatus. Ignition attempts were made as the temperature was decreased. The glass flask was not cleaned between ignitions. When the lowest point giving ignition was reached, the value was rechecked with a series of clean flasks. The self ignition temperature obtained was 125° C. Delay times up to a maximum of approximately 3 to 4 seconds were experienced.

Flash point. - The flash point was determined in a modified Pensky-Martens type closed-cup apparatus. The sample cup has a volume of only 3 cubic centimeters and is half filled with liquid sample. The temperature rise of the cup was held to less than 1° C per minute. Inasmuch as boron burns with a green colored flame, the flash could be easily seen. The flash point obtained for Hi-Cal-2 was 17° C.

Vapor pressure and decomposition. - The thermal-stability apparatus for Hi-Cal-2 consisted of a 200-milliliter cylindrical glass bulb attached to a mercury manometer with approximately 18 inches of glass capillary tubing. This tubing was wound with a nichrome heating coil to prevent condensation. A steel tube furnace fitted closely around the glass sample bulb and a thermocouple attached directly to the bulb measured the temperatures.

A sample of the Hi-Cal-2 was placed in the bulb in a helium inerted dry box. The bulb was attached to the capillary tubing and then degassed at -196° C. The bulb was next placed in the furnace and heated at the rate of approximately 30° C per hour. Pressure and temperature measurements were recorded at 15-minute intervals.

The results are shown in figure 1, where the pressure in millimeters is plotted against the temperature in °C. The pressure of the vapor is measured in the first part of the heating curve. At higher temperatures decomposition occurs and the pressure of the gaseous decomposition products is added to the pressure of the Hi-Cal-2. The dashed line in figure 1 is the expected extension of the vapor pressure curve. Finally, there is a decrease in the rate of pressure increase as the supply of liquid material is depleted.

In order to determine the temperature of incipient decomposition, the log of the pressure in millimeters is plotted against $1/T, ^\circ K$ in figure 2. The straight-line portion of the curve represents the region in which the vapor pressure alone is being measured. At about 160° C decomposition commences and adds to the total pressure. Finally, at temperatures above 270° C the supply of liquid material is depleted and the pressure levels off.

The equation for the straight-line portion of the vapor pressure curve between 50° and 160° C in figure 2 is

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$$\log P = - \frac{7825}{2.303RT} + 6.240$$

where

P pressure, millimeters of mercury

T temperature, °K

The mean molar heat of vaporization over the temperature range covered by the straight-line portion of the curve is 7825 calories. By extrapolating to a pressure of 760 millimeters of mercury the boiling point of 236° C would be obtained.

Blow-out velocity. - The blow-out velocity of Hi-Cal-2 was determined in a $1\frac{7}{8}$ -inch-diameter combustor. This combustor and the operational procedures are discussed in detail in references 4 and 5. Briefly, the apparatus consisted of an air atomizing fuel nozzle, mixing chamber, $1\frac{7}{8}$ -inch-diameter combustion chamber, pilot, and metering systems for both the air and fuel. The system was run at approximately atmospheric pressure. For the determination of the blow-out limits, the atomizing air flow and the fuel flow were held constant. The main air flow was first set low to ignite the fuel-air mixture, then gradually increased until the flame failed. The velocity at the blow-out point was computed from the air flow at a reference area ($1\frac{7}{8}$ -inch diameter) with atmospheric pressure and temperature assumed.

The results of the blow-out tests are shown in figure 3 together with the results of two reference fuels, propylene oxide and JP-4. The vertical curve for Hi-Cal-2 shows that the blow-out limit of the fuel is beyond the air capacity of the burner.

DISCUSSION

Considerable difficulty was encountered with the test sample of Hi-Cal-2 because of foreign matter in the fuel. In most cases, the filters in the transfer lines became clogged with the solid and gelatinous material, and in some cases even the by-pass lines became clogged.

The boron content and heat of combustion were sufficiently high to make the sample suitable as a fuel for engine development. Hi-Cal-2 contains sufficient boron to investigate problems associated with boron oxide deposits. The boiling point and vapor pressure correspond roughly to that of a C_{13} hydrocarbon and are thus in a range considered for aircraft fuels. Although the marked increase in viscosity at -65° C (-85° F) would probably not seriously affect engine development studies, some consideration would have to be given to possible fuel system problems that might occur under low-temperature conditions.

While the 125° C spontaneous ignition temperature is considerably lower than that found for hydrocarbons (decane and hexadecane have spontaneous ignition temperatures of about 230° C), the material can presumably be handled in air under normal conditions. No tests were made to determine if slow oxidation occurred at room temperature. The flash point (17° C) is also considerably below that of hydrocarbons of similar volatility. Tetradecane has a flash point of about 100° C. Both the relatively low self ignition temperature and flash point, however, indicate that Hi-Cal-2 would have greater reactivity with air than conventional fuels. The high reactivity of Hi-Cal-2 is further confirmed by the blow-out tests. At an equivalence ratio of 0.3, the blow-out velocity exceeded 220 feet per second, considerably above the maximum blow-out velocity of a fuel like propylene oxide. Although no quantitative relation exists between these blow-out tests and engine performance, a high blow-out velocity is usually associated with good performance in engines.

On the basis of the relatively few tests performed, it appears that a fuel having the properties of Hi-Cal-2 may be suitable for engine development if the foreign materials are removed. There is not sufficient information to determine whether the fuel is suitable for propulsion applications.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, October 5, 1955

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2. Hibbard, Robert R., and Dugger, Gordon L.: Fundamental Flame Velocity, Heat of Combustion, and Spontaneous Ignition Temperature of Dimethylaminodiborane. NACA RM E52L23, 1952.
3. Rosenblum, Louis, and Allen, Harrison, Jr.: Preparation and Physical Properties of Some Trialkylboranes. NACA RM E55E06, 1955.
4. Cook, Preston N., Jr., Lord, Albert M., and Kaye, Samuel: Blow-Out Velocities of Various Petroleum, Slurry, and Hydride Fuels in a $1\frac{7}{8}$ -Inch-Diameter Combustor. NACA RM E54A28, 1954.
5. Morris, James F., Caves, Robert M., and Lord, Albert M.: Blow-Out Velocities of Several Slurry and Liquid Fuels in a $1\frac{7}{8}$ -Inch-Diameter Combustor. NACA RM E54L27a, 1955.

TABLE I. - CHEMICAL AND PHYSICAL PROPERTIES OF HI-CAL-2

[Subscripts refer to standard deviations.]

Elemental analysis:	
Boron, percent	53.60.37
Carbon, percent	32.33.19
Hydrogen, percent	13.51.04
Total	99.44
Heat of combustion, Btu/lb	-23,159 ₄₈ (at 25° C)
Density, g/ml	0.841 at 20° C 0.838 at 25° C
Freezing point	No true one found
Self ignition temperature, °C	125
Flash point, °C	17
Vapor pressure	$\log P_{\text{mm}} = - \frac{7825}{2.303 RT_{\text{abs}}} + 6.240$
Boiling point (extrapolated), °C	236
Decomposition, °C	>160

TABLE II. - HEAT OF COMBUSTION OF HI-CAL-2

	Run 1	Run 2
Sample weight, g	0.4313	0.4746
Raw heat, Btu/lb	-21,495.0	-21,424.5
Percent carbon burned	90.0	89.9
Percent boron burned	77.5	77.5
Corrections, cal/g:		
Unburned carbon	-261.0	-264.9
Unburned boron	-1683.8	-1689.8
Hydration and solution of boron oxide	339.2	339.9
Vaporization of water	704.4	704.4
Constant volume to constant pressure	-37.0	-37.0
Correction to atmospheric pressure for oxygen consumed	-1.3	-1.4
Total corrections, cal/g	-939.5	-948.8
Btu/lb	-1691.1	-1707.8
Net heat of combustion, Btu/lb	-23,186.1	-23,132.3
Average	-23,159	

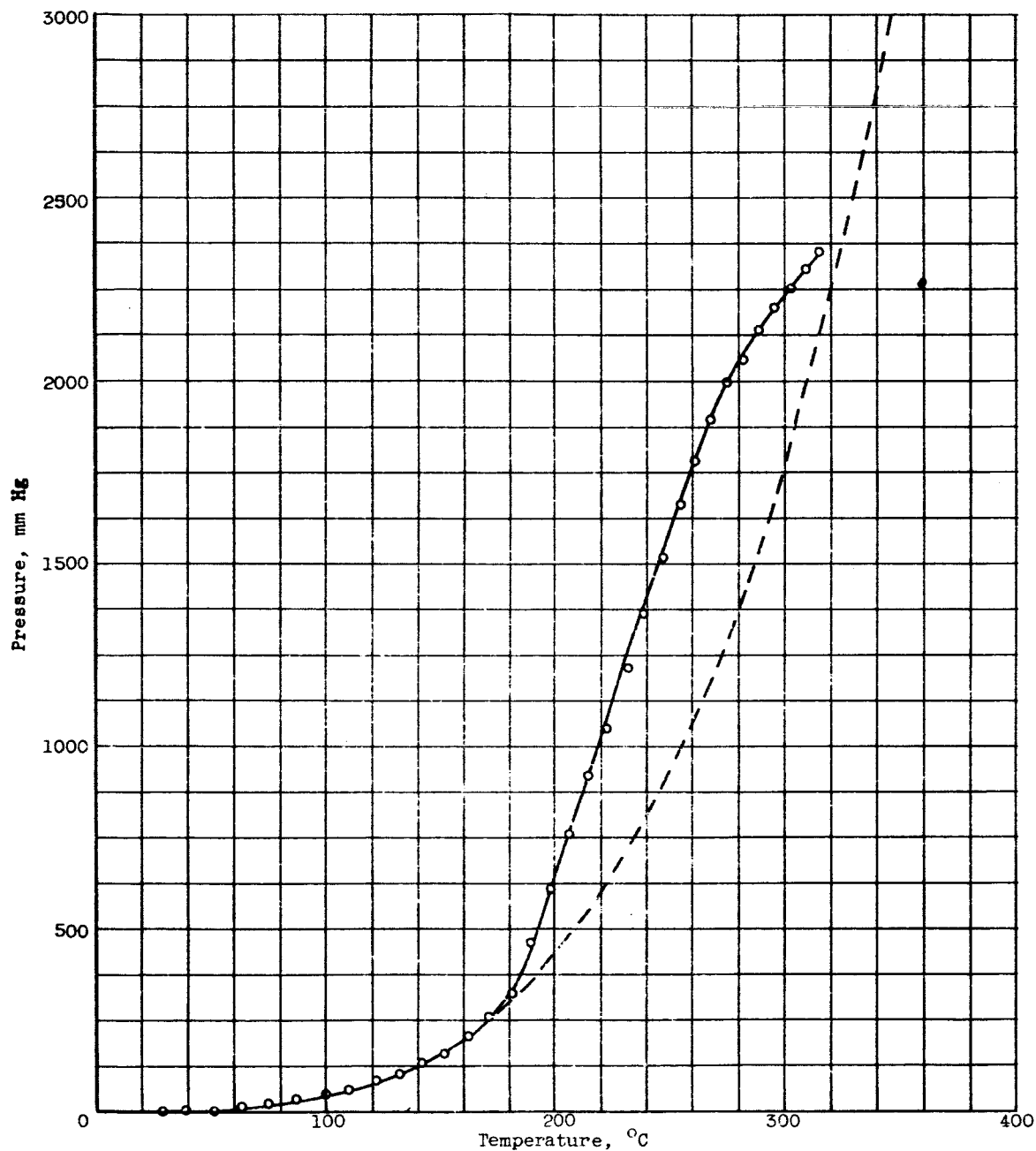


Figure 1. - Pressure developed by H1-Cal-2 with increasing temperature.

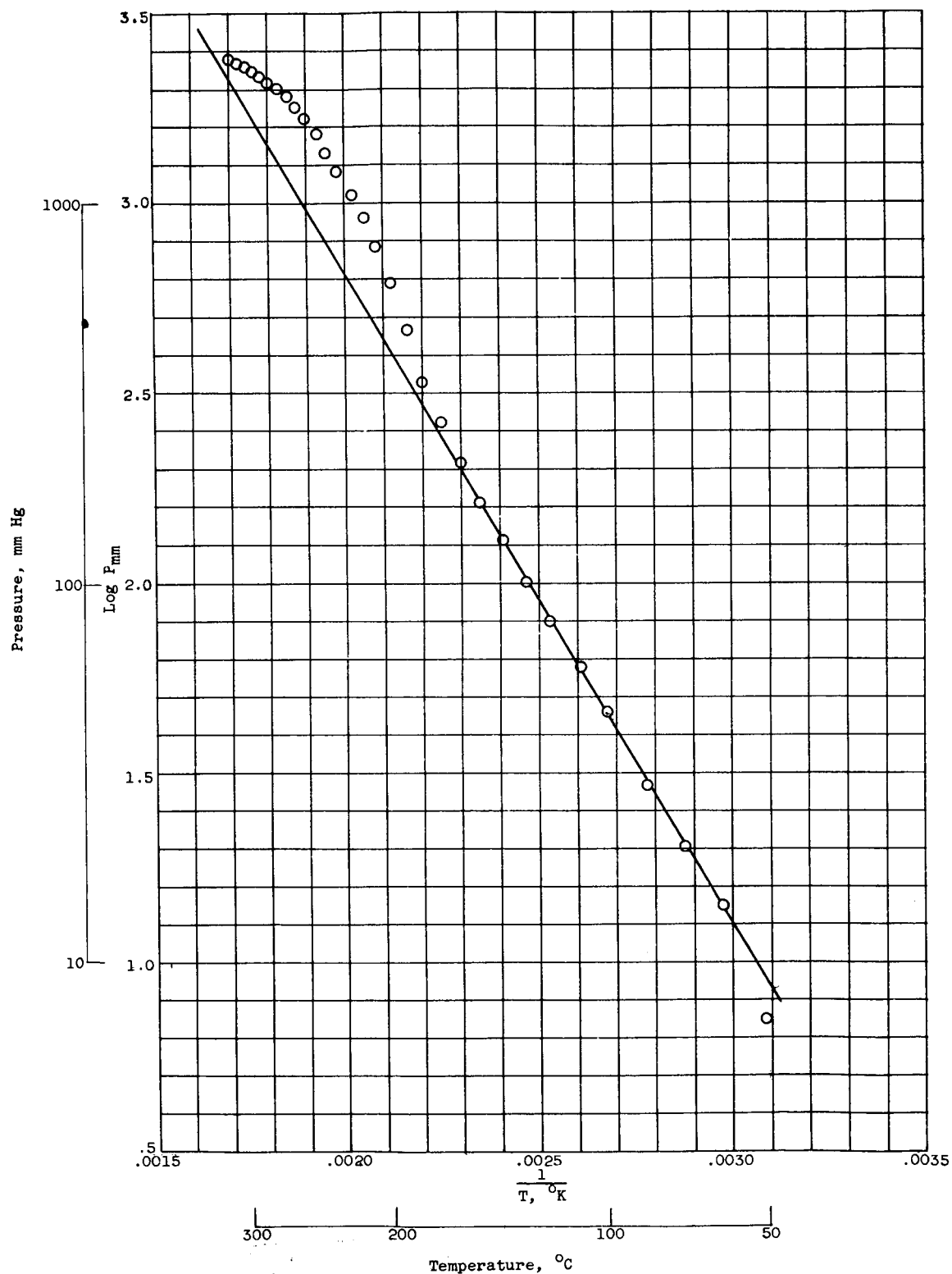


Figure 2. - Pressure-temperature relation for H1-Cal-2.

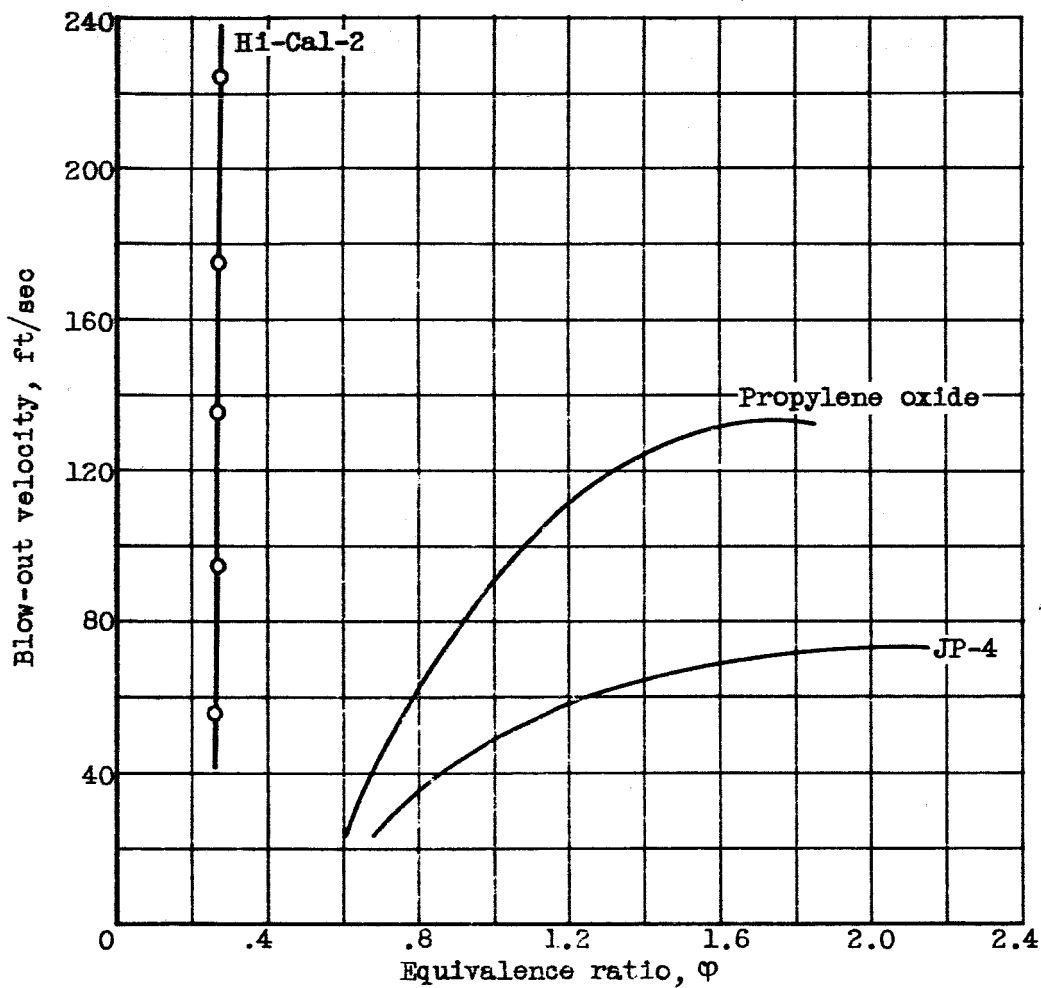


Figure 3. - Blow-out velocities of Hi-Cal-2, propylene oxide, and JP-4 in $\frac{7}{8}$ -inch-diameter combustor.

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CHEMICAL AND PHYSICAL PROPERTIES OF HI-CAL-2

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